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THERMAL DECOMPOSITION OF A DICKITE-HYDRAZINE INTERCALATION COMPLEX

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Abstract—The intercalation complex of a low-defect dickite from Tarifa, Spain, with hydrazine was studied by high-temperature X-ray diffraction (HTXRD), differential thermal analysis (DTA), and thermogravimetry (TG). The X-ray diffraction (XRD) pattern obtained at room temperature indicated that the intercalation of hydrazine and H_2O into dickite caused an increase of the basal spacing from 7.08 to 10.24 Å, which is slightly lower than the 10.4-Å spacing commonly observed after intercalation into kaolinite. Heating between 25–50°C produced a structural rearrangement of the complex, which decreased the basal spacing from 10.24 to 9.4 Å, and the resulting 9.4-Å complex was stable between 50–90°C. Heating between 90–300°C caused a gradual reduction in spacing, which occurred through a set of intermediate phases. These phases were interpreted to be interstratifications of intercalated and non-intercalated layers. These changes were also observed by DTA and TG. Two main endothermic reactions and two main stages of mass loss, respectively, were indicated in the DTA and the TG curves in the temperature range 25–200°C. This behavior suggests that intercalated molecules, hydrazine and H_2O, occupied well-defined sites in the interlayer of the dickite. The intercalated molecules were lost in an ordered fashion as confirmed by the infrared analysis of the decomposition products; H_2O was lost in the first stage and ammonia was identified in the second stage. Above 300°C, complete removal of the intercalated molecules restored the basal spacing of the dickite. However, the basal reflections were broadened, the relative intensities were changed, and changes in the dehydroxylation temperature indicated that the intercalation-desorption process induced some stacking disorder in the dickite structure.

Key Words—Dickite, DTA-TG-DTG, HTXRD, Hydrazine, Intercalation Complex, Kaolinite.

INTRODUCTION

Intercalation of hydrazine in the interlayer of kaolin minerals has been extensively studied by X-ray diffraction (XRD) and spectroscopic methods (Weiss *et al.*, 1963; Ledoux and White, 1966; Wada and Yamada, 1968; Range *et al.*, 1969; Jackson and Abdel-Kader, 1978; Theng *et al.*, 1984; Johnston, 1990; Johnston and Stone, 1990; Gábor *et al.*, 1995; Frost *et al.*, 1998; Kloprogge *et al.*, 1999; Kristóf *et al.*, 1997, 1999; Ruiz Cruz and Franco, 2000). Most of these studies involve the kaolinite-hydrazine (K-H) complex, and especially the characterization of kaolinites with various degrees of lattice disorder (*e.g.*, Range *et al.*, 1969; Fernández González *et al.*, 1976; Gábor *et al.*, 1995; Kloprogge *et al.*, 1999), whereas the dickite-hydrazine (D-H) and nacrite-hydrazine (N-H) complexes have received less attention.

XRD analyses indicate that hydrazine intercalation in the interlayer of the kaolin minerals produces a basal spacing of ~10.4 Å (Wada and Yamada, 1968). Range *et al.* (1969), however, showed that the basal spacing of the hydrazine-halloysite (H-H) complex is 10.0–10.2 Å. These authors also demonstrated that a variable fraction of the starting sample does not react with hydrazine, whereas some kaolinite specimens react slowly and lead to complexes with a basal spacing of 9.5–9.6 Å. A similar spacing was observed by Johnston and Stone (1990) during hydrazine loss at decreasing pressure, and this was interpreted as relating to the structural rearrangement caused by the loss of a portion of the intercalated hydrazine. Frost *et al.* (1998) and Kloprogge *et al.* (1999) showed XRD patterns of K-H complexes with broad basal reflections, consisting of three overlapped peaks with *d* values of 10.28, ~9.50, and ~8.80 Å. These authors proposed that the intercalation of kaolinites occurs in steps and that the spacing at 10.28 Å is caused by the incorporation of H_2O in the K-H intercalate. The observed differences in the 001 reflection profiles between high- and low-defect kaolinites upon intercalation were attributed to the defect structures. Ruiz Cruz and Franco (2000) showed that complexes with decreasing *d* values (10.4, 9.6, and 8.5 Å) appeared during removal of the intercalated molecules with increasing temperatures. They suggested that the intercalated H_2O and hydrazine occupy well-defined positions in the interlayer, which allows the ordered loss of these substances. The rate of loss of H_2O and hydrazine was assumed to be different during the destruction of the complex, as previously suggested by Kristóf *et al.* (1999). However, this assumption cannot be proved for the K-H intercalation complex because several stages of mass loss overlap.

Because dickite differs from kaolinite structurally and the D-H intercalation complex has not been previously examined in detail, we have studied the deintercalation of the D-H complex to investigate the possible differences in thermal behavior as compared to

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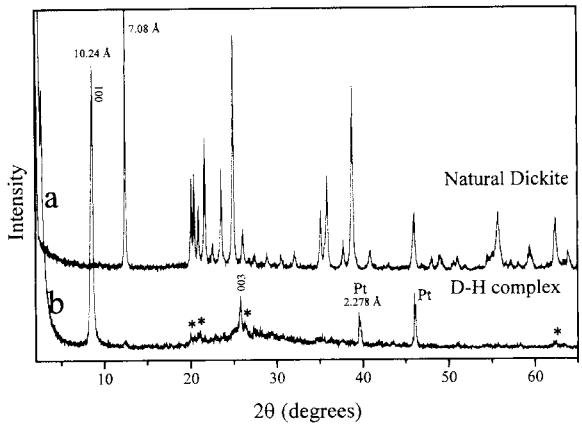


Figure 1. a) X-ray diffraction pattern of natural dickite (random clay-aggregate mount). b) X-ray diffraction pattern of the dickite-hydrazine intercalation complex obtained at room temperature with an oriented clay-aggregate mount. The more intense reflections of the complex and the reflections from the Pt holder are labeled. *shows non-basal reflections of the complex.

the K-H complex. As shown below, the behavior of the D-H complex during heating permits analysis of the thermal decomposition products and thus, verification of the proposed hypothesis.

EXPERIMENTAL

The specimen used for this study was a low-defect dickite from Tarifa, Spain. At the sampling locality, dickite fills veins as the only constituent or along with kaolinite (Ruiz Cruz and Reyes, 1998). The selected sample consists of dickite alone and no other impurities were detected by XRD (Figure 1a). Dickite occurs either as stacks of irregular plates of 5–10 μm thick or as blocky crystals of similar size. The reagent used was 98% pure hydrazine monohydrate (Prolabo Company, Fontenay, France). The D-H intercalation complex was obtained by two different methods (Johnston and Stone, 1990): 1) Dickite (0.5 g) was mixed with 10 cm^3 hydrazine monohydrate for lengths of time ranging from 1 h to 7 d. The mixture was sealed, maintained at room temperature, and the excess solution was separated by centrifugation. 2) A few drops of hydrazine were placed on an oriented sample of dickite. Natural dickite was characterized by XRD and by differential thermal analysis (DTA), thermogravimetry (TG), and differential thermogravimetry (DTG). The D-H intercalate was studied using high-temperature X-ray diffraction (HTXRD) and DTA-TG-DTG.

The wet hydrazine-treated sample was spread on a platinum (Pt) holder of a Siemens D-5000 diffractometer. The HTXRD patterns were obtained using CuKα radiation at 40 kV and 30 mA, a step size of 0.02°, and a counting time of 1 s. The heating rate was 4°C/s. The samples heated to a particular temperature were held at that temperature for 600 s prior to the XRD pattern being acquired. Diffractograms were obtained after variable temperature intervals (between 5–50°C) according to the expected modifications indicated by the DTA-TG-DTG curves. The Pt reflection at 2.28 Å was used as a standard peak to determine *d* values. Thermal analyses were performed in a Rigaku-Thermoflex apparatus (TG-8110) provided with a TASS 1000 station. Al_2O_3 was used as reference material. DTA, TG, and DTG curves were recorded simultaneously in static air at heating rates of 10, 5, or 1°C/min. The thermal behavior of the complex at a heating rate of 10°C/min was also investigated in a helium atmosphere with a Shimazu TGA-50H instrument connected to an infrared (IR) spectrometer (Nicolet Magna) and a mass spectrometer (Fisons Thermolab). This system allowed an accurate identification of the decomposition products.

RESULTS

The near complete expansion of the dickite structure from a basal spacing of 7.08–10.24 Å (Figure 1) was obtained after 2-d reaction with hydrazine. Intercalation of hydrazine into dickite was slow compared to the reaction with Cornwall kaolinite (Ruiz Cruz and Franco, 2000), where almost complete intercalation occurred after 1-h treatment. This difference is probably a consequence of the larger size of the dickite particles relative to the kaolinite grains. Moreover, the basal spacing is lower for the D-H complex. The complex has a sharp 001 reflection and a weak 003 reflection (Figure 1b). All indices for the complex are referred to a one-layer structure, similar to the presentation of Ruiz Cruz and Franco (2000) for the K-H complex. This pattern shows weak non-basal reflections because it was obtained from an imperfectly oriented sample. A wide diffraction band centered at ~26 °2θ is probably related to excess hydrazine. The reflections at 2.28, 1.97, and 1.38 Å are from the Pt holder.

The DTA curve of the D-H complex obtained at a heating rate of 5°C/min (Figure 2, trace c) shows two well-defined endothermic peaks centered at 63 and 118°C and a higher temperature, weak peak at 168°C. In the curve obtained at the heating rate of 10°C/min (not shown in Figure 2), the temperatures of the two main endothermic peaks are higher (82 and 138°C), and the second one is followed by an exothermic peak. The DTA curve obtained at the heating rate of 1°C/min (not shown in Figure 2) was similar to that shown in Figure 2, but the various peaks were notably less well defined. At higher temperatures, the DTA curves of the D-H complex show a broad endothermic peak centered at 615, 573, or 570°C, depending on the heating rate, and an exothermic peak in the range 984–990°C. Moreover, two weak peaks were observed in the range 200–300°C and were more evident in the curves obtained at the heating rate of 10°C/min. The

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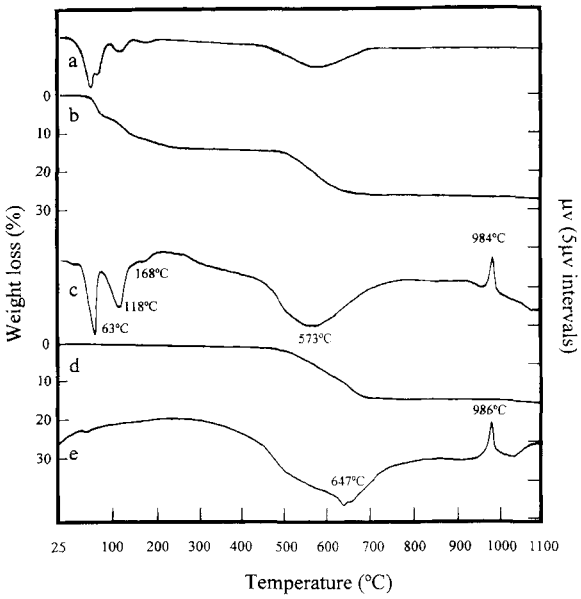


Figure 2. DTA-TG-DTG curves of the dickite-hydrazine intercalation complex, obtained at a heating rate of 5°C/min and DTA-TG curves of dickite obtained under similar conditions. a) DTG curve of the complex. b) TG curve of the complex. c) DTA curve of the complex. d) TG curve of dickite. e) DTA curve of dickite.

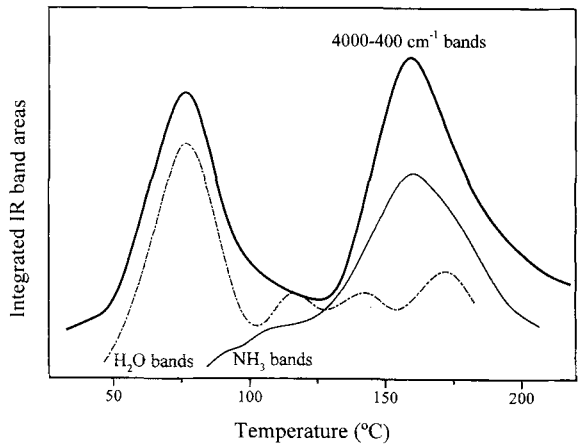


Figure 3. Variation of the integrated areas of the IR bands of H_2O (between 3946–3807 cm^{-1}) and IR bands of NH_3 (between 975–925 cm^{-1}) in the temperature range of 20–200°C obtained at a heating rate of 10°C/min. The bold line represents the sum of the contributions of the H_2O and NH_3 bands.

low-temperature DTA endothermic effects are accounted for by two main stages of mass loss observed in the TG and DTG curves (Figure 2, traces b and a). Thus, these curves indicate that the loss of H_2O + hydrazine occurs in separate steps. The weak peak observed in the DTA curve at 168°C probably corresponds to the loss of strongly bonded molecules, as indicated by the small but continuous mass loss observed in the TG curve in this temperature range. Wada and Yamada (1968) also reported the fixation of a portion of the intercalated hydrazine with its complete removal at 200–300°C. The endothermic peak centered at ~600°C corresponds to the dehydroxylation of dickite as revealed by the mass loss observed near this temperature in the TG curve. This peak occurred at slightly lower temperatures than those observed in the DTA-TG curves of the untreated dickite (Figure 2, traces d and e). A dickite/(H_2O + hydrazine) ratio of about 1:2 in the initial complex was estimated from the mass loss measured in these stages. This ratio is higher than the 1:2.6 to 1:3 ratio estimated by Kristóf *et al.* (1999). The exothermic peak observed at ~990°C probably represents structural changes in the metadickite structure, because only a wide band centered at ~4.23 Å was observed in the XRD patterns obtained after heating at 1000°C.

The IR analysis of the products formed during the heating of the D-H complex under He atmosphere also confirmed the two main stages of mass loss at low temperatures observed in the DTA curves. The variation of the integrated areas of the OH bands (for H_2O) and NH bands (for hydrazine) (Figure 3) indicates that H_2O was mainly lost at <100°C, whereas above this temperature only small H_2O loss is observed. In contrast, NH_3 was lost between 125–200°C. This temperature range coincides with that of the second endothermic effect observed in the DTA curve of the complex obtained at a heating rate of 10°C/min. This behavior was not observed during heating of the K-H complex, in which H_2O and hydrazine were nearly simultaneously released from the complex (Kristóf *et al.*, 1999; Ruiz Cruz and Franco, 2000).

The most significant HTXRD patterns of the D-H complex (Figure 4) revealed that the intensity of the 7-Å reflection of dickite increased regularly from 40 to 300°C. The HTXRD patterns permitted the distinction of two main stages of removal of the intercalated molecules: 1) In the first stage below 50°C, the loss of some of the intercalated molecules leads to a reduction in the basal spacing of the complex from 10.28 to 9.41 Å. 2) In a second stage between 90–300°C, further desorption caused continuous broadening and shifted the 9.4-Å reflection to 7.22 Å.

The pattern obtained at 70°C (Figure 5) revealed that the complex with a basal spacing of 9.49 Å showed a set of basal reflections (both odd and even) with *d* values slightly lower than those observed in the patterns of the K-H complex obtained in this temperature range (Ruiz Cruz and Franco, 2000). The HTXRD patterns between 90–300°C (Figure 6) illustrated the second stage of removal of the intercalated molecules. A notable sharpening of the 7.20-Å reflection was observed in the pattern obtained at 300°C. The gradual contraction of the basal spacing of the complex from 9.41 to 7.20 Å was accompanied by the

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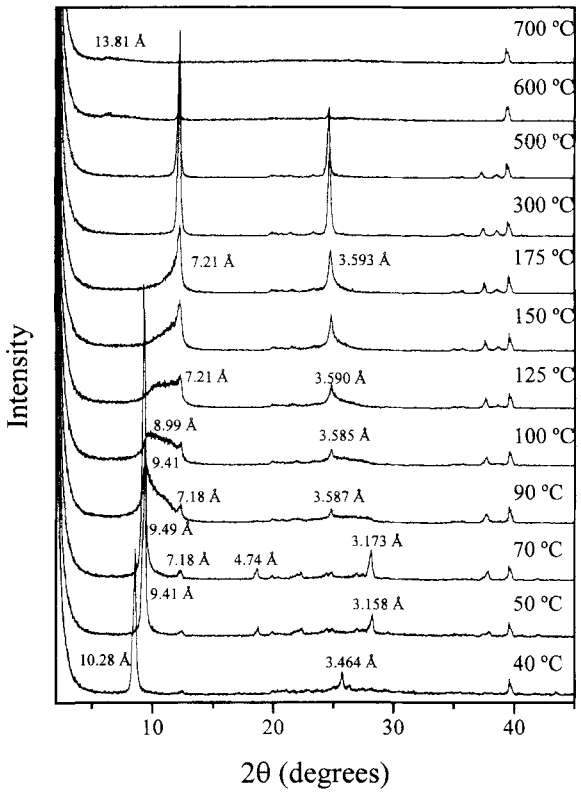


Figure 4. Selected HTXRD patterns obtained after heating in the range of 25–700°C.

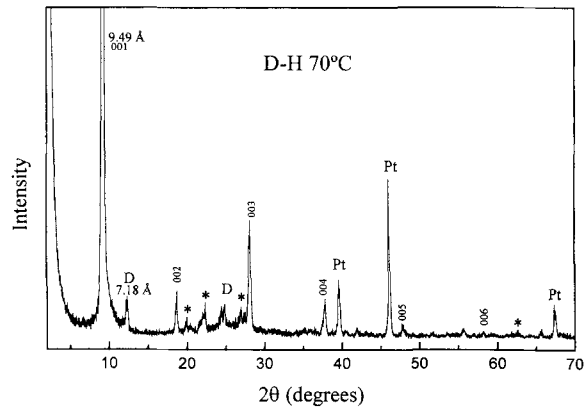


Figure 5. HTXRD pattern obtained after heating at 70°C. The more intense reflections of the 9.49-Å complex are labeled. D: dickite reflections. *shows non-basal reflections of the 9.49-Å complex.

complete desorption of hydrazine from a fraction of the complex, as indicated by a gradual increase in intensity of the 7.20-Å reflection of dickite from 90 to 300°C.

The HTXRD patterns obtained in the 500–700°C range (Figure 7) revealed a gradual decrease in intensity of the dickite reflections which were absent in the pattern obtained at 700°C. These patterns showed some broadening of the basal reflections of the dickite relative to those of the untreated sample. The number of 14-Å dickite layers as determined by XRD and using the Scherrer formula (Rodríguez Gallego, 1982) decreased from 37 in the untreated dickite to ~20 in the restored dickite. Nevertheless, broadening was less than that observed after destruction of the complex with kaolinite (Ruiz Cruz and Franco, 2000). In addition, these patterns revealed a significant decrease in intensity of the 004 reflection relative to the 002 reflection of the dickite. The dehydroxylation of dickite also caused the appearance of a broad diffraction band with a maximum at ~13.5 Å.

DISCUSSION

The X-ray pattern of the D-H complex obtained at room temperature (Figure 1d) as well as the DTA-TG curves and the HTXRD patterns (Figures 2 and 4) showed some differences from the patterns of the K-H complex described by Ruiz Cruz and Franco (2000). The differences were mainly in *d* values and the temperatures at which the intercalated molecules were desorbed. Thus, intercalation of hydrazine in dickite produced a complex with a 10.24-Å spacing, which is

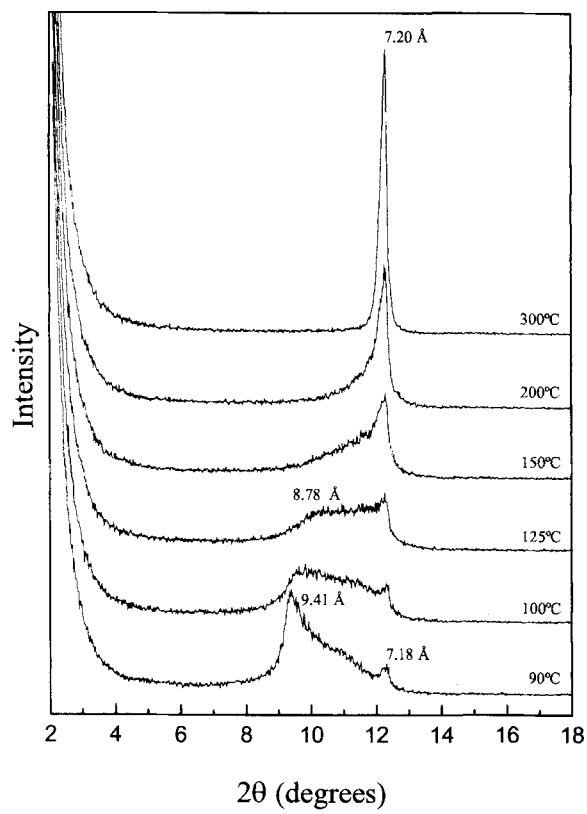


Figure 6. Selected HTXRD patterns obtained in the range of 90–300°C showing the gradual shift of the basal reflection of the intercalate.

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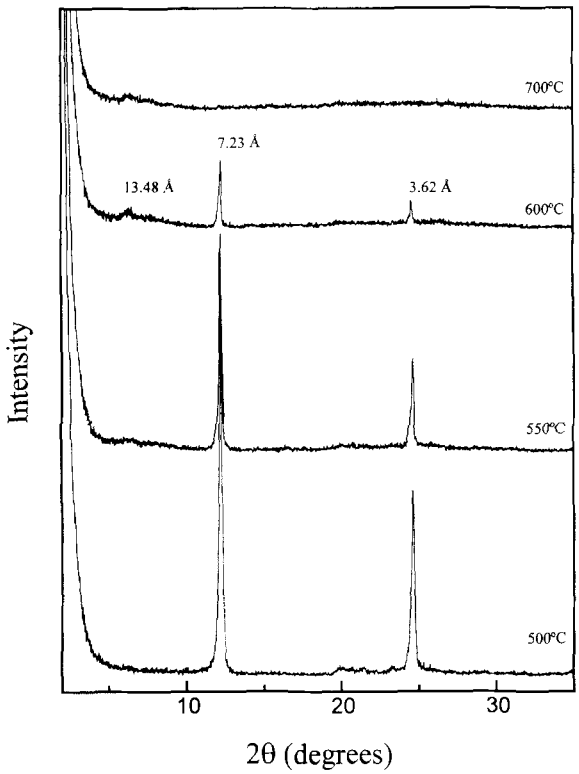


Figure 7. Selected HTXRD patterns obtained between 500–700°C, showing the behavior of the basal reflections of dickite.

lower than the 10.4-Å spacing commonly observed in the K-H complex. This difference was related, at least in part, to the different basal spacings of the untreated dickite and kaolinite which were, respectively, 7.08 and 7.14 Å. Moreover, the basal spacings of this type of intercalation complex seem to show some variation even in kaolinites, and values of 10.27–10.28 Å have also been found in K-H complexes (Frost *et al.*, 1998; Kloprogge *et al.*, 1999). As in the case of the K-H complex, the presence of well-defined, non-basal reflections in the range $2\theta = 20–25°$ suggests the formation of a three-dimensionally ordered intercalate.

The first stage of desorption of the intercalated molecules leads to a shift of the basal reflection of the complex from 10.28 to 9.4 Å (Figure 4). This reduction occurred above 50°C in the K-H complex and between 40–50°C in the D-H complex. These differences in temperature probably depend on the degree of drying of the complex. It appears that elimination of the adsorbed H_2O + hydrazine causes contraction of the complex. Despite the lack of coincidence in temperatures, this reduction in *d* value is correlated with the first stage of mass loss in the TG curve and the first endothermic peak in the DTA curve. This intermediate intercalation complex also showed a *d* value slightly lower than the 9.6 Å measured in the K-H complex. This "contracted" complex was observed by Johnston and Stone (1990) during hydrazine loss at decreasing pressure and interpreted, from IR spectra, as owing to the keying of the hydrazine molecules into the ditrigonal cavities of the tetrahedral sheet. Recently, Frost *et al.* (1998) and Kloprogge *et al.* (1999) proposed that intercalation takes place in steps. The 9.48-Å spacing was interpreted as the intercalation of the hydrazine and the 10.28-Å spacing as the incorporation of H_2O into the intercalate. Our results indicate, however, that intercalation of hydrazine into kaolinite and dickite always causes a sharp reflection (between 10.2–10.4 Å), whereas the structural modifications occur during destruction of the complex. The IR analysis of the products formed during heating of the complex indicates that the first stage of mass loss mainly corresponds to the liberation of H_2O. This confirms the hypothesis of Frost *et al.* (1998), Kloprogge *et al.* (1999), and Ruiz Cruz and Franco (2000) that the complex with a basal spacing of 10.2–10.4 Å contains both H_2O and hydrazine in the interlayer, as well as the assumption by Ruiz Cruz and Franco (2000) that H_2O and hydrazine are lost in separate stages.

The structural changes induced by H_2O loss are reflected in the X-ray patterns of the 9.4-Å complex of D-H mainly by the presence of both odd and even basal reflections, and are similar to those of the 9.6-Å complex of K-H. This structurally ordered complex was stable only within a narrow temperature interval below 90°C.

Differences in thermal behavior between the D-H and K-H complexes were sharper in the temperature range of 80–175°C, where the K-H complex basal spacing contracted to 8.5 Å (Ruiz Cruz and Franco, 2000). This intermediate complex was not observed in the HTXRD patterns of the D-H complex, which showed complete loss of the intercalated species during collapse of the 9.4-Å complex through intermediate structures. The intermediate structures probably consisted of random interstratifications of both intercalated and non-intercalated dickite sequences. This second structural change is correlated with the second stage of mass loss observed in the TG curve and with the second (high temperature) endothermic peak in the DTA curve. The IR analysis of the products liberated in this second stage indicates that the high-temperature mass loss was mainly NH_3, which corresponds to hydrazine liberation.

As in the case of the K-H complex (Ruiz Cruz and Franco, 2000), the successive structural modifications suggest that the intercalated molecules present in the complex obtained at room temperature occupied well-defined positions in the interlayer of the dickite and that they were lost in an ordered fashion. This hypothesis is confirmed by the IR analysis of the decomposition products. The mass loss measured in the TG curve indicates a dickite : hydrazine : water ratio of 1:

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1:1. The following interpretation is reasonable: The 10.24-Å spacing observed at room temperature corresponds to the intercalation of one hydrazine layer + one H_2O layer. The hydrazine molecules are probably keyed into the ditrigonal cavities of the siloxane surface of the dickite and form strong H bonds as assumed in previous interpretations (*e.g.,* Ledoux and White, 1966), whereas the H_2O layer is probably H bonded to the OH surface. The rapid loss of the weaker-bonded H_2O molecules yielded the 9.4-Å complex that was observed at increasing temperatures and would only contain hydrazine in the interlayer. From 90°C and above, the slower loss of the hydrazine molecules leads to interstratifications of intercalated and non-intercalated dickite layers. The gradual increase of non-intercalated dickite layers caused a shift in the basal spacing. Finally, the small mass loss observed at ~170°C represents the loss of more strongly bonded residual molecules.

This behavior is different from that observed for the K-H complex (Ruiz Cruz and Franco, 2000), where the partial loss of hydrazine caused a decrease of the basal spacing to 8.5 Å. This probably represents, as suggested by Frost *et al.* (1998) and Kloprogge *et al.* (1999), a change in orientation of the hydrazine molecules.

Heating above 300°C (Figures 4 and 7) caused a progressive increase in the stacking order of dickite as revealed by both sharpening and intensity increases in the 002 dickite reflection. Nevertheless, this reflection is significantly broader than that of untreated dickite. Thus, the number of layers in the diffracting domains decreased as a consequence of the intercalation-desorption processes, which was noted by Barrios *et al.* (1977) from a study of the K-H complex.

The HTXRD patterns obtained between 500–600°C (Figures 4 and 7) revealed that the dickite reflections gradually decrease. The increase in disorder coincided with the dehydroxylation temperature of the dickite, which was lower than that observed for untreated dickite.

CONCLUDING REMARKS

The HTXRD patterns of the D-H intercalation complex indicated that removal of the intercalated species below 50°C occurred through an ordered complex with a sharp reflection at 9.4 Å. Loss of the intercalated molecules between 90–300°C was gradual and was indicated by a broad diffraction band between 9–7 Å. This behavior suggests that the intercalated molecules occupied well-defined positions in the interlayer of the dickite and that their loss was based on relative bonding strength. The analysis of the thermal decomposition products confirms that the weakly bonded H_2O molecules were lost in a first stage, whereas most of the hydrazine loss occurred in a second stage.

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